EFFECT OF DEHYDRATION ON THE SPECIFIC HEAT OF CHEESE WHEY

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ABSTRACT

Differential scanning calorimetry was used to determine the specific heat of cheddar cheese whey as a function of water content and thereby provide fundamental data useful for the further development of dried whey products. The specific heat of fluid cheddar cheese whey, which contains 7% solids, was 0.951 ± .036 cal/g/°C at 12°C. A linear relationship was maintained between specific heat and moisture content when dried whey solids were rehydrated to moisture levels between 3 and 93% H_2O. The apparent partial specific heat of the whey solids was 0.328 cal/g/°C and that of the water was 0.995 cal/g/°C, a value close to that of bulk water. An inflection, however, was noted in the relation between specific heat and water content at 50% H_2O when the specific heat data were obtained with concentrated whey samples prepared by evaporation of water from fluid whey. These data yielded apparent partial specific heat values for water of 0.966 cal/g/°C above 50% H_2O and 1.203 cal/g/°C below 50% H_2O. Apparently the water is in a more structured form in concentrated systems provided that the solids are initially fully hydrated. This conforms to the concept that a critical amount of water must be present in a proteinaceous system for the water to be held in a quasi-solid or "icelike" structure.

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INTRODUCTION

Much of the nutritious solids in whey have been wasted in the past. However, recent legislation to reduce environmental pollution has discouraged this practice. Considerable quantities of whey are now being spray-dried for use as feed and food. This process, however, is relatively inefficient, at least partly because the various dissolved and suspended materials in liquid cheese whey bind substantial quantities of water. With the prospect of serious energy shortages it is becoming increasingly important for scientists to obtain thermodynamic data which should be useful to the developers of more efficient food processing techniques. In this study the relationship between water content and the specific heat of cheddar cheese whey was determined, both to define a portion of the energy requirements in whey processing and to provide an insight into the physical chemical state of water in concentrated whey.

We have reported (1) on the specific heat of β-lactoglobulin, the major whey protein, containing 20-250 mg sorbed water per gram protein. Whey is a more complex system containing carbohydrate and salt fractions which also bind substantial quantities of water (2). We have now extended our studies with the differential scanning calorimeter to measure the specific heat of cheddar cheese whey over a wide range of water contents from anhydrous whey solids to ordinary fluid whey, containing 93% water. We investigated the reversibility of the water binding process by measuring the changes in specific heat accompanying the dehydration of fluid whey and the rehydration of whey powder.

EXPERIMENTAL

Materials. A single lot of cheddar cheese whey powder, spray dried in the Dairy Products Laboratory Pilot Plant, was used throughout this study to insure identity of the solid components in all samples. Moisture levels in powder samples up to 0.25g H_2O/g whey solids were adjusted by exposing the powder to controlled humidity environments, maintained with appropriate saturated salt solutions (3). Samples at higher moisture levels were prepared by dispersing the whey powder in water to form preparations ranging from concentrated slurries to dilute solutions.

To study the properties of fluid whey, powder was reconstituted to 7% total solids content and held overnight to allow for completion of lactose mutarotation. Reconstitution of the dried whey was preferred over using separate batches of fluid whey that might vary slightly in composition. The reconstituted whey was concentrated with a rotary evaporator and/or freeze-dried to obtain whey samples at various stages of dehydration.

Methods. Specific heats were determined using the Perkin-Elmer Model DSC-1B[1] differential scanning calorimeter by a technique based on the methods of Wunderlich (4) and O'Neill (5). First, empty sealed aluminum capsules were heated in the sample and reference holders of the calorimeter from 0 to 25°C at a programmed rate of 5°C/min. to establish a baseline accounting for the asymmetry of the system as a function of temperature. The power output of the calorimeter was then calibrated by replacing the empty capsule on the sample holder with one containing a 0.03g sample of Al_2O_3 (standard sapphire plate supplied by the Perkin-Elmer Co.) and repeating the scan from 0 to 25°C at 5°C/min. Finally, this capsule was replaced with one containing a whey sample (5-35 mg), and the scan was repeated to determine the specific heat. Cooling below ambient temperature was accomplished by filling the low temperature cover of the DSC-1B with solid CO_2. More stable recorder tracings were obtained when solid CO_2 was used rather than liquid N_2, and there were less of the usual experimental nuisances resulting from moisture condensation on the instrument.

The sample pans used in these determinations were hermetically sealed with the Perkin-Elmer volatile-sample sealer accessory to prevent the condensation or evaporation of water vapor until after the completion of the specific heat determination. After the scan, the moisture content of each sample was determined by puncturing the sample container and drying to constant weight under vacuum at 65°C.

Experimental specific heats were calculated from the amplitudes of the recorder tracings using sapphire specific heat data of Ginnings and Furukawa (6). The sample and reference pans used were weighed and selected so that the specific heat of aluminum could be neglected. Apparent partial specific heats were determined using the equation of White and Benson (7), as employed by Bull and Breese (8) in the form:

$$(1 + W_1)\ C_p = \bar{C}_{p_2} + \bar{C}_{p_1}\ W_1$$

where W_1 is the weight of water per gram of whey solids, C_p is the experimental specific heat for whey solids plus water, $\bar{C}_{p_1}$ is the apparent partial specific heat of the water, and $\bar{C}_{p_2}$ is the partial specific heat of the whey solids.

Results and Discussion. The specific heat of the reconstituted fluid cheddar cheese whey was found to be 0.951 ± .036

[1]The mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

cal/g/°C at 12°C. This value is the average of four separate determinations and the error indicated here and elsewhere in this paper is the standard deviation. This value and the other specific heat data presented in this paper are only the values computed for 12°C, the mid-point of the DSC scans; however, specific heats were computed at 5° intervals between 7 and 22°C. No significant variation in specific heat with temperature was observable in this range for any of the whey samples. The data at temperatures other than 12°C have therefore not been reported in detail.

It is not unexpected that the specific heat of fluid whey is similar to that of water since fluid whey is approximately 93% water. Accordingly, when water is removed from whey during concentration or drying, the specific heat value is diminished. Such changes in specific heat during the course of dehydration are evident from the data in Figure 1 where the specific heats of whey samples are presented graphically as a function of moisture content.

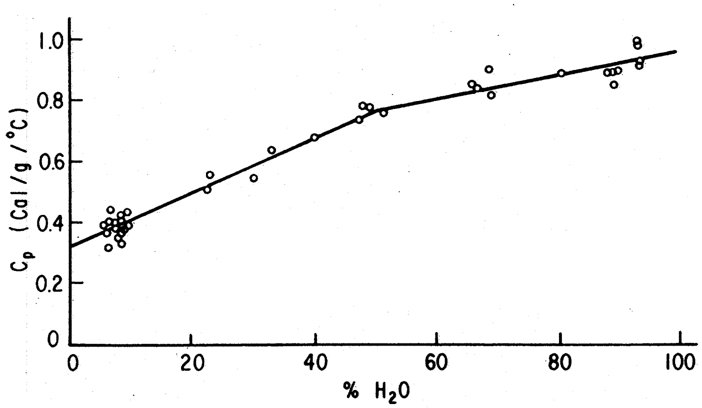

Figure 1. Graph of C_p, the measured specific heat of concentrated and dehydrated whey at 12°C against percent water

Examination of these data indicates an inflection in the relation between specific heat and water content occurring at about 0.5g of water per gram of sample. Bull and Breese (8) reported a similar inflection in the relation between specific heat and the water content of ovalbumin crystals at 0.43g H_2O/g egg albumin. In our studies (1) with crystalline ovalbumin and β-lactoglobulin only linear relationships between specific heat and water content were observed; however, those studies were limited to systems containing less than 25% water.

When dried whey was rewetted to various levels of rehydration, a linear relation between heat capacity and water content was maintained over the entire range from zero to 93% water (Figure 2). Least squares analysis of these data yielded the linear relation:

$$C_p=0.312 + 0.007\ (\%\ H_2O).$$

In this equation C_p represents the measured specific heat of the whey solids-water samples, and the intercept on the C_p axis at

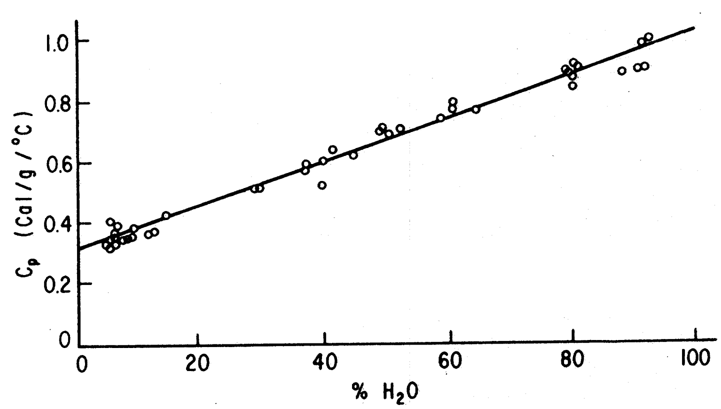

Figure 2. Graph of C_p, the measured specific heat of rehydrated whey solids at 12°C against percent water.

zero water content is the extrapolated value for the specific heat of anhydrous whey solids, i.e. 0.312 cal/g/°C. A similar value of 0.315 cal/g/°C was obtained from the data in Figure 1 for whey samples which were dehydrated to less than 50% moisture. Analysis of the data of Figure 1 yielded the equations:

$$C_p = 0.315 + 0.009\ (\%\ H_2O)$$

for samples containing 0-50% H_2O and

$$C_p = 0.562 + 0.004\ (\%\ H_2O)$$

for the more dilute samples.

Comparison of these two sets of data for hydration and dehydration clearly suggest the presence of some fundamental physical difference in these processes. Further insight into these phenomena may be obtained from the apparent partial specific heats of the water and the whey solids in each case. Plots of $(1+W_1)\ C_p$ against W_1 were made for: (1) the experimental points (Fig. 1) in the range from zero moisture to the inflection point, (2) the experimental points (Fig. 1) in the range from the inflection point to 93% moisture, and (3) all the data (Fig. 2) for rewetting the dried whey solids. The results of these plots, analyzed by least squares, are given in Table 1 with the variations expressed as the standard deviations.

Table 1: Apparent partial specific heat values for water, $\bar{C}_{p_1}$, and whey solids, $\bar{C}_{p_2}$.

Sample and moisture range	$\bar{C}_{p_1}$ (cal/g/°C)	$\bar{C}_{p_2}$ (cal/g/°C)
Dehydrated whey, 0-50% H_2O	1.203 ± .028	0.316 ± .012
Concentrated whey, 50-93% H_2O	0.966 ± .020	0.467 ± .151
Rehydrated whey, 0-93% H_2O	0.995 ± .010	0.328 ± .046

It is notable that when whey is concentrated to less than 50% moisture, there is an appreciable increase in the apparent partial specific heat of the water associated with the whey solids over that of water in the bulk. Bull and Breese (8) reported a value of 1.247 ± .023 cal/g/°C for the apparent partial specific heat of water associated with ovalbumin, and they attributed the increase over the specific heat of bulk water to the large exothermic heat of hydration of egg albumin. Heating a sorbate-sorbent combination at constant pressure usually results in the desorption of gas or vapor if the system is initially at equilibrium, thereby complicating heat capacity measurements of adsorbed films by unwanted desorption effects which cause the coverage to be temperature dependent and the total heat capacity to increase above the isosteric value (9). In a previous publication (1) we demonstrated that heat capacities of protein-water systems measured with the differential scanning calorimeter using sealed containers are isosteric values. We concluded from the isosteric specific heat values, $\bar{C}_{p_1}$, for water sorbed by ovalbumin (1.269 $\pm$ .103 cal/g/°C) and β-lactoglobulin (0.947 $\pm$ .137 cal/g/°C) that the sorbed water exists in some structured form involving multiple hydrogen bonding. The excess heat capacity of liquid water over that of ice or water vapor is sometimes called "structural" heat capacity, and is attributed to the thermal breakdown of the associated structure present in the liquid (10). Water molecules bound to isolated specific sites on the surface of a protein should not exhibit such a structural heat capacity contribution, hence the elevation of $\bar{C}_{p_1}$ over that of ice or water may be taken as evidence for the association of sorbed water into a structured hydration shell. The results with ovalbumin (1) and our present data for concentrated and dehydrated whey (< 50% H_2O) suggest an even greater order of structuring of the associated water in these systems. In more dilute systems (> 50% H_2O) it is conceivable that so much water is present as ordinary water in addition to that associated with the whey solids that the apparent partial specific heat approaches that of bulk water.

The similarity between $\bar{C}_{p_1}$ for water associated with whey solids rehydrated to less than 50% water (Table 1) and the specific heat of bulk water demonstrated that no excess structure is present unless the whey solids are more completely hydrated. Changes in specific heat of biological materials during hydration are not unusual. Chakrabarti and Johnson (11) measured the specific heat of tobacco-water complexes with the differential scanning calorimeter and observed inflections in the specific heat-moisture content relation above 40% H_2O. A transitional moisture range was identified which they related to a change in water from an adsorbed phase to a solution phase. Similarly, elevated heats of desorption of water vapor from milk and whey powders at higher moisture levels have been reported (12).

While studying water binding in proteinaceous systems (13) we observed an increase in the heat of vaporization of sorbed water once a critical amount of water (approximately 0.18g H_2O/g protein) is sorbed by β-lactoglobulin, bovine serum albumin, bovine casein, or calfskin collagen. It was concluded that at the higher moisture levels the solid protein matrix had become swollen, and possibly conformational changes occurred in the protein molecules permitting more H_2O - surface contacts and ultimately the formation of a quasi-solid or "icelike" structure. It is thus plausible that excess structuring of associated water in whey only occurs at higher moisture levels and is observable upon dehydration from such dilute systems. Interactions of water with other components of the whey solids should, however, not be neglected.

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